

Effect of Reaction Temperature on the Structural and Optical Properties of ZnO Nanocrystals

A. Parra-Palomino, R. Singhal, *O. Perales-Perez, C. Sotomayor, Paul Voyles¹, M. S. Tomar and W. Jia

University of Puerto Rico, Mayaguez, PR 00680-9044, *ojuan@uprm.edu

¹University of Wisconsin, WI – 53706 -1595.

ABSTRACT

In order to study systematically the dependence of ZnO crystal size with synthesis conditions, stable suspensions of these nanocrystals were produced in ethanol at temperatures between 0°C and 60°C. XRD characterization of solid products verified the formation of ZnO nanocrystals with no need for any thermal treatment even at a temperature as low as 0°C. The significant shift in the position of the XRD peaks in those samples synthesized at different temperatures and aging times, suggested a systematic variation in the dimensions of the ZnO unit cell. FT-IR spectra of washed ZnO crystals showed the bands attributed to acetate species, which are considered to be adsorbed onto the nanocrystals surface. The high monodispersity of the 5-8nm ZnO nanocrystals was revealed by HRTEM analyses of the samples synthesized at room temperature. Lower temperatures of synthesis were conducive to smaller nanocrystal sizes. UV-Vis and PL measurements evidenced the continuous growth of the nanocrystals during aging.

Keywords: ZnO, nanocrystals, temperature effect, quantum confinement.

1 INTRODUCTION

Highly monodisperse nanocrystalline materials are extensively studied due to their size-dependent functional properties. Semiconductor nanoparticles are expected to show quantum confinement effect when their size is become comparable to the Bohr exciton radius, which result in an increase in the energy gap relative to that of the material bulk. For instance, the quantum confinement effect and the strong size-dependence of the optical properties have been verified for different nanosize semiconductors [1-3]. ZnO, a II-VI type semiconductor, having a wide band gap of 3.29eV and a direct band gap structure at room temperature is considered a very promising material for optoelectronic and spintronics applications. Several nanosize semiconductor particles have been produced by different synthesis routes. For instance, synthesis inside reverse micelles has been developed to control the shape and size of the nanoparticles [4]. Among the different solution synthesis approaches, the use of ethanol -not only as a solvent but also as a dehydrating agent- has permitted the production of oxide nanocrystals with excellent

structural and optical properties [5]. This method was extended to doped-ZnO systems [6, 7]. The possibility of restricting crystal growth when nanocrystals are aged in mother liquors at room-temperature was also verified [8]. On this basis, the present work investigated the effect of the reaction temperature on the formation of ZnO crystals in ethanol solution to determine the corresponding structural and optical properties as a function of the crystal size at the nanoscale.

2 EXPERIMENTAL

2.1 Synthesis of Nanocrystals

ZnO nanocrystals were synthesized by conventional precipitation in ethanol solutions as reported by Spanhel and Anderson [5]. In our case, the synthesis process involves the preparation of nanoparticles at different temperatures ranging from 0°C to 60°C. A 0.1M Zinc acetate ($ZnC_4H_6O_4 \cdot 2H_2O$, Aldrich) solution was prepared in ethanol at 65 °C. Lithium hydroxide ($LiOH \cdot H_2O$, Strem Chemicals), was added to the Zn solution to make a final concentration of 0.14M Li. Resulting solution was mixed at different temperatures for 10 minutes. In order to follow the progress of the oxide formation, the suspension of nanocrystals were aged in their mother liquors for different times. The aging stage took place at the same temperature of synthesis. Nanocrystals prepared by this route were coagulated in n-heptane, washed twice with fresh ethanol and dried at 40°C for 24 hours.

2.2 Characterization Techniques

The structural characterization of synthesized solids was performed in a Siemens D5000 X-Ray diffractometer (XRD) using the $CuK\alpha$ ($\lambda=0.15405$ nm) radiation. FT-IR spectra were recorded with DIGILAB FTS 1000 SCIMITAR Series Fourier transform infrared spectrophotometer. The optical absorption properties of stable suspensions of nanocrystals en ethanol were determined from UV-Vis spectroscopy using a Beckman Coulter DU800 spectrophotometer. Luminescence spectra were recorded under ambient conditions in a Fluoromax-2, ISA, Jobin-Yvon. Raman spectra were obtained using a Jobin-Yvon T64000 Raman spectrometer.

3 RESULTS AND DISCUSSION

3.1 XRD Characterization

Figure 1 shows the X-ray diffraction patterns of ZnO nanocrystals synthesized at 0°C and different aging times.

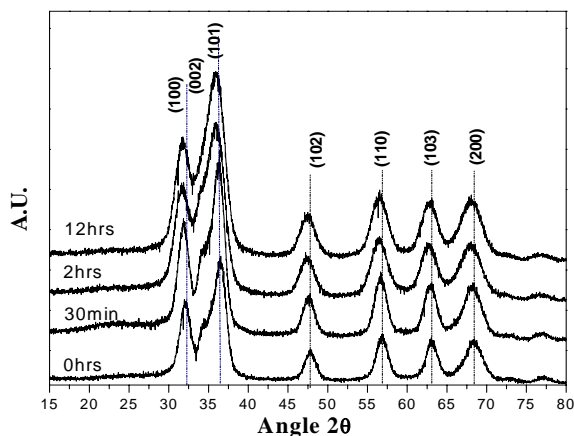


Figure 1: XRD patterns ZnO nanocrystals synthesized at 0°C and different aging times.

The absence of any peaks other than those corresponding to ZnO, suggests the formation of the oxide structure even with no aging (0 minutes). It was observed a significant shift in the peaks angular positions, which may suggest a progressive variation in ZnO lattice parameters. The 'a' and 'c' lattice parameters varied from 3.2161 Å to 3.2377 Å and from 5.2037 Å to 5.228 Å when the samples were produced after 0 minutes and 12 hours of aging, respectively. XRD patterns of non aged ZnO nanocrystals, synthesized at different temperatures are shown in Figure 2. All peaks correspond to ZnO wurtzite structure. Also in this case, a gradual shift on the peaks towards lower diffraction angles with a rising temperature was observed. The lattice parameter 'a' and 'c' for the solids prepared to 60°C varied to 3.239 Å to 5.235 Å. The sharpening in XRD peaks, observed in those samples produced at higher temperatures evidences the enhancement of ZnO crystallinity with a rising temperature of synthesis. The average crystallite size of the nanocrystals was found to vary between 2.7 nm and 8 nm as the synthesis temperature increases from 0°C to 60°C. From the previous information, it becomes clear a direct relationship between average crystallite size and unit cell dimensions: the smaller the crystallite size, the shorter the unit cell dimensions. A change in cell parameters by a decrease in crystallite size has also been observed for other oxide systems [9]. Moreover, a contraction in unit cell could be expected for ionic oxides as ZnO [10]. This effect was attributed to the strong size-dependence of long-range Coulomb forces and cooperative phenomena involved with

the stability of a crystal and the equilibrium lattice parameters.

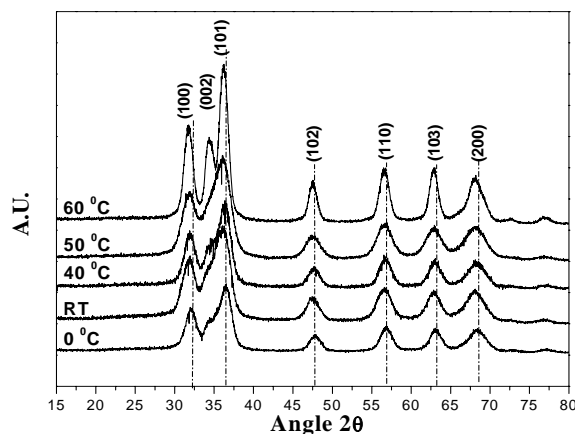


Figure 2: XRD patterns for ZnO synthesized at different temperatures.

3.2 FT-IR Measurements

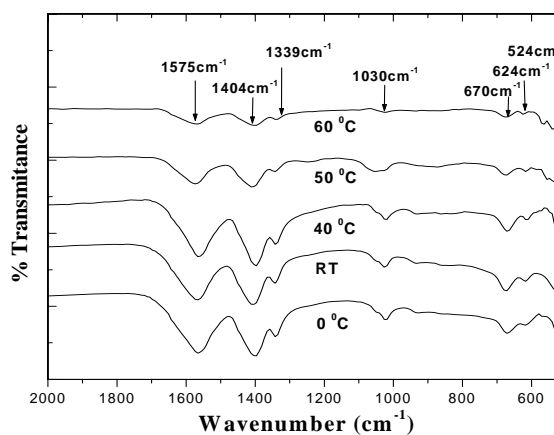


Figure 3: FT-IR spectra of non-aged ZnO crystals synthesized at different temperatures.

Figure 3 shows the FTIR spectra of non-aged ZnO crystals synthesized at different temperatures. The band centered at 525 cm^{-1} corresponds to the stretching vibrations of the Zn-O bonds and evidences the development of the ZnO structure. The bands at 624, 670, 1030, 1339, 1404, and 1575 cm^{-1} , are due to the stretching vibration of C=O, C=C and C-H groups in acetate species, which are considered to be adsorbed onto the nanocrystals surface.

3.3 HRTEM Observations

HRTEM analyses were performed on samples of ZnO nanocrystals synthesized at room temperature and aged for 20 minutes (Figure 4). Darker particles show stronger diffraction due to orientation. The nanoparticles were highly monodisperse, with sizes between 6 and 8 nm, and well-crystallized. Nanometric sizes of the particles are

attributed to the very fast nucleation rate capable to be reached during synthesis in ethanol. Also, adsorbed acetate species must have provided a net negative charge to the surface of the nanocrystals that prevented their aggregation.

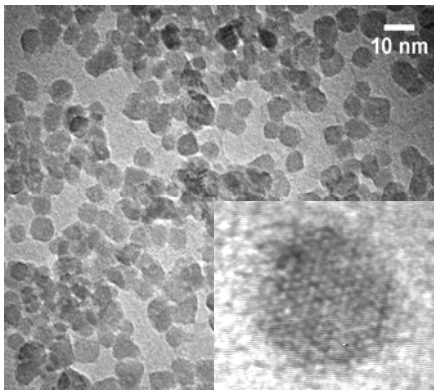


Figure 4: ZnO nanocrystals synthesized at room temperature and aged for 20 minutes. The inset shows a single nanocrystal.

3.4 UV-Vis and PL Measurements

Figure 5 shows the UV-Vis absorption spectra taken from a stable suspension of ZnO nanocrystals synthesized at 0°C and aged in their mother liquor at the same temperature.

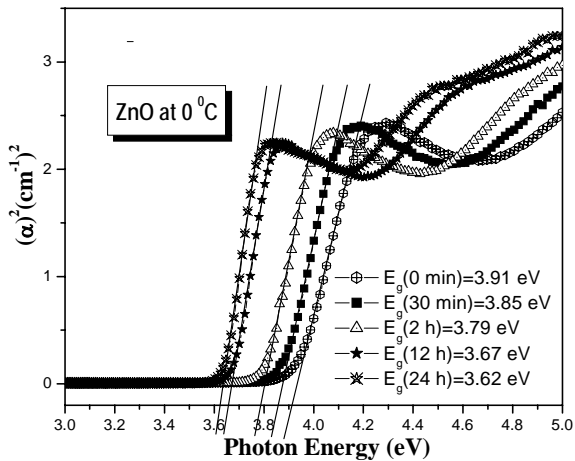


Figure 5: UV-vis spectra of ZnO nanocrystals synthesized at 0°C and different aging times.

The red shift observed in absorption peaks with prolonged aging time suggests the progressive increase in particle size. Large band gap energy values (above 3.6 eV) are due to the high quantum confinement effect in extremely small crystallite sizes. The band gap energy for bulk ZnO is 3.29 eV. The crystal growth observed during aging time could be stopped by coagulation with n-heptane.

Emission spectra of ZnO nanocrystals synthesized at 0°C withdrawn at different aging and redispersed in fresh ethanol are shown in Figure 6. These measurements were carried out at room-temperature. The emission band centered at 513 nm (2.42 eV) was shifted to 527 nm (2.34 eV) upon crystal growth taking place during aging.

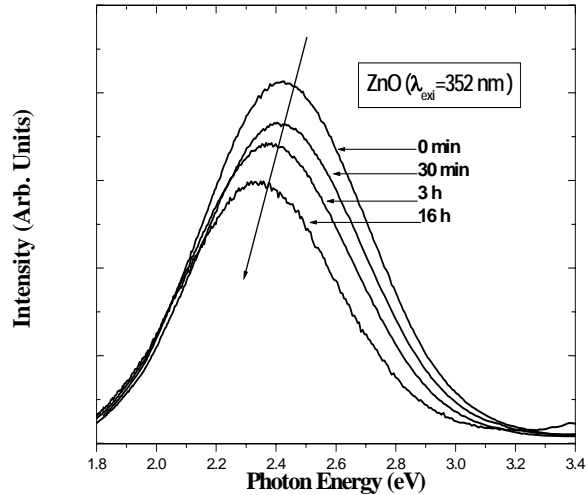


Figure 6: Emission spectra of ZnO synthesized at 0°C and aged for different times ($\lambda_{\text{excitation}} = 352 \text{ nm}$).

These visible emission peaks can be attributed to surface traps, oxygen vacancies or the incorporation of Li^+ ions at ZnO interstitials.

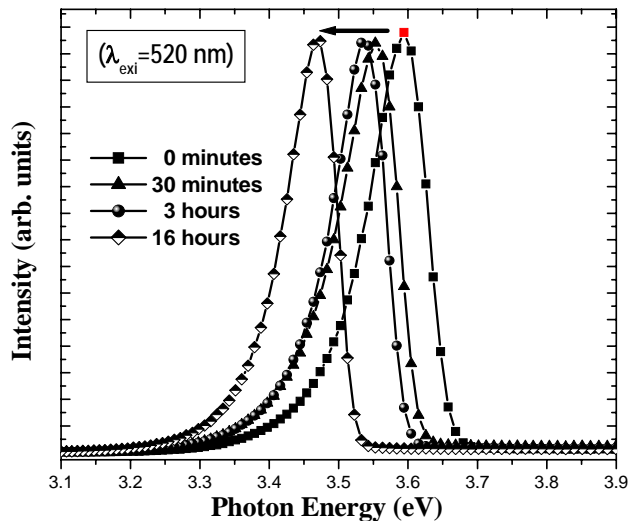


Figure 7: Emission spectra of ZnO synthesized at room-temperature and aged at different times. The $\lambda_{\text{excitation}}$ was 520nm.

Figure 7 shows the UV emission spectra for ZnO nanocrystals synthesized at room temperature. A shift in the UV emission peak centered at 345 nm (3.59 eV) to 357 nm (3.74 eV) was also observed upon crystal growth during

aging. High efficient UV emission near to the band edge is attributing to free exciton emission with high electronic density of the states [11], which shift to higher energies when the nanocrystals size decrease from 8 to 2.7 nm. In general, quantum confinement shifts the energy levels of the conduction and valence band giving rise to a blue shift in the transition energy as the particle size decrease. Similar behavior were also been found in another semiconductor materials [12].

4 CONCLUDING REMARKS

We have successfully synthesized ZnO nanocrystals in ethanol in the temperature range between 0°C and 60°C. No aging was needed for the formation of oxide structure. As expected, crystal growth –and hence, a dramatic change in optical behavior- could be promoted by increasing temperature during synthesis. XRD and FT-IR analyses verified the nanocrystalline nature of the produced powders and the direct dependence between the crystal size and the synthesis conditions. The crystallinity of produced nanoparticles was also confirmed by HRTEM observations that also revealed a high monodispersity of ZnO nanoparticles in the range of 5-9 nm. When the change in crystal size was not apparent from XRD observations, UV-Vis measurements evidenced that the higher the synthesis temperature, the lower the band gap, and hence, the bigger the crystal size. Photoluminescence (PL) confirmed the nanocrystalline nature of produced ZnO. The high intensity of green luminescence, which is associated to surface traps in the ZnO nanocrystals, needs further investigation about the root cause.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 0351449. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation (NSF). Thanks are also extended to NSF-Start Up Program for providing support for part of this research.

REFERENCES

- [1]H. Borchet et al. J. Chem. Phys. Vol 119. pp 1800-1806. 2003
- [2]Dmitri V. Talapin, Andrey L Rogach, Andreas Kornowski, Markus Hasse, Horst Weller. Nanoletters. Vol 1. pp 207-211. 2001
- [3]B.O. Dabbousi. J. Phys. Chem. B. Vol 101. pp 463-9475. 1997.
- [4]Fang J, Wang J, Ng S C, Chew C H and Gan L M. Nanostruct. Mater. Vol. 8. pp. 499. 1997.
- [5]L. Sphangel and M. A. Anderson, J. Am. Chem. Soc. Vol 113. pp. 2826. 1991.

- [6]P.V. Radonvanoic, N. S. Norberg, K.E. McNally and D. R. Gamelin. J. Am. Chem. Soc., Vol 124. pp. 15192. 2002.
- [7]D. A. Schwartz, N. S. Norberg, Q.P. Nguyen, J.M.Parker and D.R. Gamelin. . J. Am. Chem. Soc., Vol 125. pp 13205. 2003.
- [8]S.P. Singh, O. Perales-Perez, M.S. Tomar, A. Parra-Palomino and A. Ruiz-Mendoza. Technical Proceedings Nanotechnology Conference. Vol 2. pp 29-32. 2005.
- [9]P. Ayyub, V. Palkar, S. Chattopadhyay et al. Phys. Rev. B, 51, 9. pp. 6135-6138. 2005.
- [10] J. E. Lennard-Jones, Z. Crystallogr. Vol 75. pp. 215. 1930.
- [11] K.-F. Lin et al. Chem. Phys. Lett. Vol. 409. pp 208-211. 2005
- [12] D.J. Norris, Al.L. Efros, M. Rosen, M.G. Bawendy. Phys. Rev. B. Vol 53. pp. 16338. 1996.